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A TECHNICAL REVIEW OF ELECTROCHEMICAL TECHNIQUES APPLIED TO MICROBIOLOGICALLY INFLUENCED CORROSION

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Abstract—A critical review of the literature concerned with the application of electrochemical techniques in the study of microbiologically influenced corrosion (MIC) is presented. The electrochemical techniques covered in this review include measurements of the corrosion potential, the redox potential, the polarization resistance, the electrochemical impedance, electrochemical noise, and polarization curves including pitting scans. For each experimental technique some discussion concerning experimental procedures, advantages and disadvantages of the technique for the study of MIC is presented. Applications range from studies of the corrosion of steel pipes in the presence of sulfate reducing bacteria to investigations of the formation of biofilms and calcareous deposits on stainless steels in seawater and the destruction of concrete pipes in sewers by microorganisms producing very low pH solutions. For each experimental technique at least one example for typical experimental data is presented.

INTRODUCTION

MICROBIOLOGICALLY influenced corrosion (MIC) has received increased attention by corrosion scientists and engineers in recent years. MIC is due to the presence of microorganisms on a metal surface which leads to changes in the rates and sometimes also the types of the electrochemical reactions which are involved in the corrosion processes. It is therefore not surprising that many attempts have been made to use electrochemical techniques to study the details of MIC and to determine its mechanisms. Applications have ranged from MIC of many structural materials in seawater to soils, aircraft fuels and sewers.

The evidence provided so far suggests that the presence of microorganisms on metal surfaces often results in highly localized changes of the concentration of some of the electrolyte constituents, pH and oxygen levels.[1,2] For passive metals these localized changes can lead to localized corrosion in the form of pitting or crevice corrosion. As with other corrosion systems, difficulties exist in the interpretation of electrochemical data obtained for cases of localized corrosion. The prevailing approach to estimate the tendency towards localized corrosion based on pitting potentials rather than to determine rates of localized corrosion often prevents advances in this area.

Electrochemical techniques have been shown to be very useful for mechanistic studies in laboratory investigations and for monitoring purposes in field studies. As with all studies of corrosion phenomena more detailed and reliable information can be obtained when a number of different electrochemical techniques are combined.

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In the special case of MIC it is of course necessary to use microbiological in addition to surface analytical techniques such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). These considerations lead to the conclusion that real advances in the understanding of the mechanisms of MIC can only be expected from the work of teams which consist of experts in the various techniques discussed above.

Dexter et al.[3] have recently presented their conclusions concerning the use and limitations of electrochemical techniques for investigating MIC. Their review focused mainly on the background of different electrochemical techniques and presented the authors' understanding of the advantages and possible problems with the techniques which are routinely used in corrosion studies. The aim of the present review is to focus on the information obtained so far with the use of electrochemical techniques in investigations of MIC and to use these results as a basis for a discussion of the type of information which can be obtained with each of these techniques. The present review is based on a computerized literature search which produced over 100 papers and the results of the authors' on-going research in the area of MIC. The following discussion is based mainly on papers published after 1970 when more systematic studies of MIC were reported.

RESULTS OBTAINED WITH ELECTROCHEMICAL TECHNIQUES IN THE STUDY OF MIC

In the following the background of the electrochemical techniques which are considered suitable for the study of MIC will be summarized briefly and some important experimental aspects will be discussed for each technique. This will be followed by a summary of the experimental results obtained so far with each technique for different metals and alloys in various environments. A critical assessment of the information obtained will be given if this is possible from an analysis of the data presented by the authors.

The corrosion potential

Measurement of the corrosion potential E_{corr} is the easiest electrochemical test, but it provides the least amount of mechanistic information. The measurement of E_{corr} requires a stable reference electrode, a high impedance voltmeter and in most cases a suitable recording device. The possibility of problems with the proper functioning of the reference electrode due to the formation of a biofilm has apparently not received much attention.

The main problem with the use of E_{corr} measurements is the overinterpretation of such data. This will be illustrated for the case of stainless steels in seawater as discussed below. Based on the information obtained with E_{corr} alone it is not possible to determine whether corrosion rates have increased or decreased. It is therefore advisable to determine not only E_{corr}, but also the polarization resistance R_P at the same time. The changes of both parameters can then be interpreted in terms of changes in the rates of the anodic and/or the cathodic partial reactions which determine the corrosion rate.

Early measurements of E_{corr} which were carried out for steel in the presence of sulfate reducing bacteria (SRB) suffer from the lack of additional information and are therefore difficult to interpret. Different authors have explained the observed
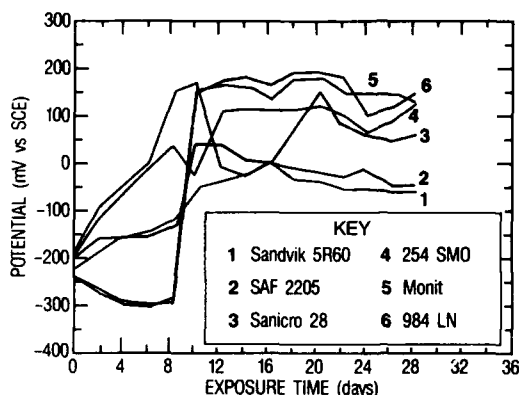
FIG. 1.   Open-circuit potential vs time for six stainless steels exposed to flowing natural seawater.[8]

changes of E_{corr} in the negative direction by a reduction of the rate of cathodic reaction[4] and by an increase of the rate of the anodic reactions.[5] These are the two simplest possibilities which can be expected to lead to the observed result. However, without additional data no valid conclusions concerning the effect of SRBs on electrochemical corrosion reactions can be drawn. Only when the exact mechanism of MIC has been established for a given system will it be possible to use E_{corr} data for monitoring purposes such as the detection of an increase of uniform corrosion rates or the initiation of localized corrosion due to the presence of bacteria.

Numerous reports have appeared in which the time dependence of E_{corr} has been monitored for stainless steels in natural seawater. Most published data show a rapid ennoblement of E_{corr} during the first days of exposure.[6-13] Figure 1 shows as a representative example potential–time curves reported by Johnsen and Bardal[8] for several stainless steels in flowing (0.5 m s^{-1}) natural seawater. E_{corr} changed from -200 to -250 mV(SCE) at the beginning of the test to -50 mV for two of the alloys and to $+200$ mV for the remaining four alloys after 28 days. Johnsen and Bardal[8] offered a different interpretation than Mollica[6] for the cause of the observed ennoblement of E_{corr}, but agreed that this effect was caused by a change of the cathodic properties of the stainless steels as a result of microbiological activity on the surface.

Dexter and Gao[12] have recently reported E_{corr} data and polarization curves for SS 316 exposed to natural seawater. The authors concluded that the observed scatter of the E_{corr} data in seawater was due to the presence of microorganisms. However in a subsequent discussion of these data[14] it became apparent that the very negative E_{corr} values for some, but not all, of the samples were due to crevice corrosion under a lacquer and should therefore be discarded. Based on the results obtained with cathodic polarization curves Dexter and Gao[12] concluded that the increase of E_{corr} for the remaining samples of SS 316 was due to an increase of the rate of the cathodic reduction of oxygen at a given potential. In an analysis of the results of the various authors who have reported an ennoblement of E_{corr} for stainless steels during exposure to natural seawater, one has to consider that these results do not demonstrate directly an increased susceptibility to corrosion. In fact, the sustained noble potentials show that the stainless steel surface retained its normal corrosion resist-

ance in seawater for the time of the experiment used by different authors. If localized corrosion would have occurred, E_{corr} would have dropped to the active potentials typical of pitted stainless steels such as the samples of Dexter and Gao[12] which suffered from crevice corrosion.

As far as the mechanism responsible for the ennoblement of E_{corr} is concerned, it is not possible from the experimental data for E_{corr} or the polarization curves to decide whether the increase of E_{corr} is due to thermodynamic effects, kinetic effects or both. The reversible potential of the oxygen reduction reaction can increase both due to a local increase of the oxygen concentration or a decrease of pH. The complexity of this situation is illustrated by the fact that naturally occurring microorganisms within a marine biofilm can decrease or increase the local oxygen concentration and pH. Little et al.[2,15] have reported some of the first measurements of the interfacial chemistry and have demonstrated its impact on the development of E_{corr} with exposure time. An increase of the exchange current density for the oxygen reduction reaction would also lead to an increase of E_{corr}. Since E_{corr} is a mixed potential, one has to consider that its value can also change due to changes in the passive current density (c.d.) of the stainless steel. At constant kinetics of the oxygen reduction reaction, E_{corr} would become more noble if the passive c.d. would decrease with exposure time. This discussion shows that a simple measurement of E_{corr} cannot provide enough information for mechanistic interpretations.

The groups of Little and Mansfeld have shown recently[2,16] that details of the exposure conditions can have pronounced effects on the constituents of the biofilm, interfacial chemistry and the resulting E_{corr}. In exposure to flowing natural seawater it was found for the stainless steels SS 304, SS 316 and SS AL6X and for Ti grade 2 that E_{corr} did not change very much over a period of four months (Fig. 2).[16] This result which is quite different from the results of other authors discussed above[6-13] was considered to be due to the exposure under reduced light conditions and the resulting very low population density of photosynthetic, oxygen-producing diatoms in the biofilm. The surface properties of these samples have been further characterized by electrochemical impedance spectroscopy (EIS) as discussed below and by SEM with EDAX.[16] No evidence of localized corrosion was detected on any of the samples exposed to Pacific Ocean water for four months. Laboratory tests for the same materials in sterile media such as NaCl and artificial seawater produced an ennoblement of E_{corr} in a few days.[17]

The discussion presented above has focused on measurements of E_{corr} for stainless steels in natural seawater. Additional E_{corr} data have been reported for mild steel in the presence of SRB which is an important topic due to the problems with localized corrosion of buried steel pipes.[18-20] Kasahara and Kajiyama[18] have presented an interesting application of the combination of electrochemical techniques such as the recording of E_{corr}, linear polarization and impedance data for monitoring purposes. E_{corr} data have also been used in the evaluation of the corrosion problems caused by fungal attack of Al alloys used as tanks for aircraft fuel.[21]

The redox potential

The reduction–oxidation (redox) or solution potential which is usually measured on an inert electrode such as Pt is an indicator of the oxidation power of the electrolyte. It could be used as an indicator of the corrosivity of the electrolyte if

suitable calibration were provided. In fact, measurements of the redox potential have been used to monitor changes in the corrosive properties of solutions as a result of the bacterial metabolism. However, it has to be realized that a solution of a given corrosivity, i.e. redox potential, can produce varying degrees of corrosion for different metals such as mild steel, stainless steel or Al exposed to the same solution. Statements such as 'another potential useful for predicting whether or not a given metal will suffer an increase in corrosion due to microorganisms is the reduction–oxidation (or redox) potential of the environment'[13] are therefore to be considered with great caution. A useful application of the redox potential would be in a combination with measurements of E_{corr} and R_p for monitoring purposes. For the assessment of potential problems with MIC in soils the combination of measurements of the redox potential, soil conductivity and water content seems to have provided useful information in the past.[22]

It has been suggested recently to use a combination of a prepassivated Pt electrode and the material of interest to follow the development of the biofilm and determine its effects on the corrosion behavior of structural materials.[23] The time dependence of E_{corr} of several stainless steels and Ti has been compared to the open-circuit potential of the prepassivated Pt electrode. Figure 3 shows the time dependence of E_{corr} for SS 304L in a solution with and without A6F bacteria, while
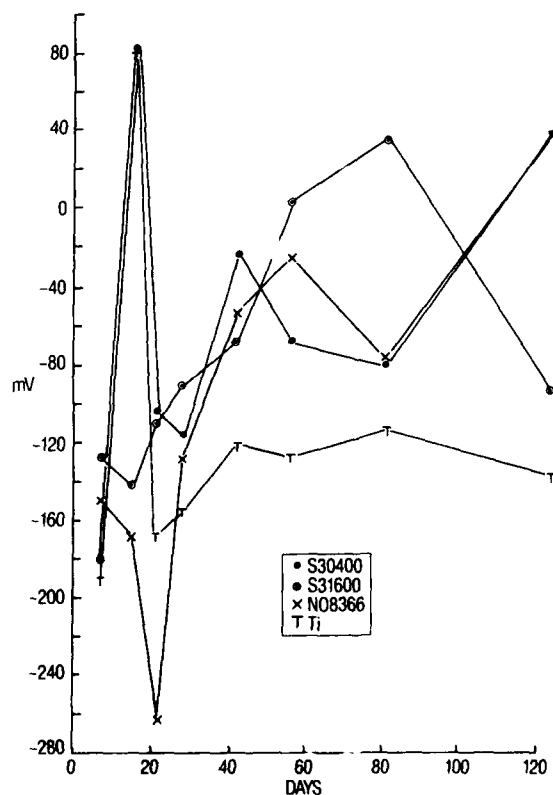

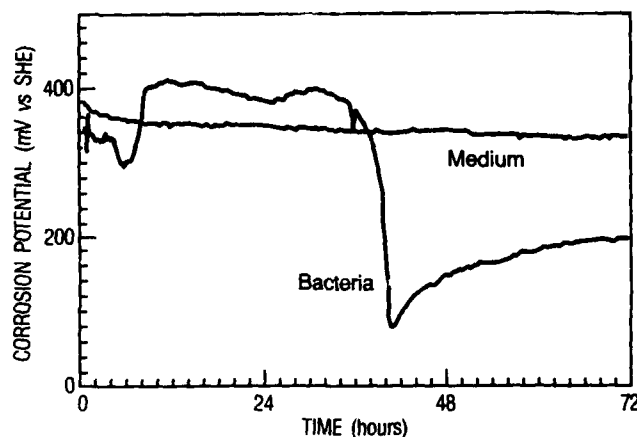Fig. 2. Open-circuit potential vs time for three stainless steels and Ti grade 2 exposed flowing natural seawater.[16]

F. Mansfeld and B. Little

Fig. 4 shows the corresponding data for Pt.[23] The authors concluded that the data shown in Fig. 3 and 4 reflect the processes of bacterial growth, changes of the local environment induced by the metabolic activities of the bacteria and the resulting corrosion effects of the metal. The role of the Pt electrode was to indicate changes in the local oxygen concentration which were assumed to be the same as those on the stainless steel under investigation. Since the potential of Pt changes in the positive direction when the oxygen concentration is increased or the pH is decreased, a pH indicator was added to the solution to determine independently the pH changes.[23] The dependence of the reversible potential of the oxygen electrode ($E^{\circ}_{O_2}$) on pH or the partial pressure of oxygen (p_{O_2}) at 25°C is given by:

$$(dE^{\circ}_{O_2})/(d\,pH)_{O_2} = -59\,mV \tag{1a}$$

$$(dE^{\circ}_{O_2})/(d\,\log p_{O_2})_{pH} = +15\,mV. \tag{1b}$$
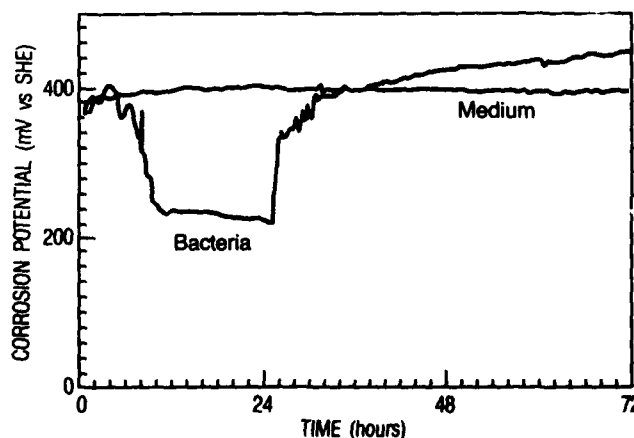
An increase of the local oxygen concentration at the electrode surface is therefore expected to produce only a small shift of the potential of a Pt electrode which is used as a redox electrode, especially since only parts of the surface are usually covered with microorganisms and experience increases of p_{O_2}.

The polarization resistance technique

The main advantage of the polarization resistance technique is the possibility to continuously monitor the instantaneous corrosion rate of a metal exposed to a corrosive environment.[24] Therefore this technique is very suitable for the detection of changes in corrosion rates due to the presence of bacteria, inhibitors, sunlight, biocides, etc. As with the measurement of E_{corr}, a persistent problem with the use of R_p data is the tendency to overinterpret the experimental data as exact corrosion rates.

A thorough review of the use of the polarization resistance technique for the measurement of corrosion currents has been given earlier.[24] R_p is defined as:

$$R_p = (\partial E/\partial i)_{i=0}. \tag{2}$$

The value R_p should therefore be measured as the slope of a potential E–current density i curve at E_{corr}, where $i = 0$. The c.d. i_{corr} is calculated from R_p by:

$$i_{corr} = B/R_p, \tag{3a}$$

where

$$B = b_a b_c/2.303(b_a + b_c). \tag{3b}$$

The exact calculation of i_{corr} for a given time during an experiment requires therefore the simultaneous measurements of R_p and the Tafel slopes b_a and b_c for this time. Computer programs such as CORFIT,[25] POLCURR[26] and POLFIT[27] have been developed by Mansfeld and co-workers for the determination of precise values of i_{corr} according to equation (3). In the analysis of experimental R_p' data, it has to be recognized that these measurements contain a contribution from the uncompensated solution resistance R_u.[24]

$$R_p' = R_p + R_u. \tag{4}$$

For electrolytes of low conductivity or systems with very high corrosion rates (low R_p) significant errors in the calculation of corrosion rates can occur if a correction for R_u is not applied. The corrosion rate will be underestimated in these cases. Additional problems can arise from the effects of the sweep rate which is used to determine R_p according to equation (2). If the sweep rate is too high, the experimental value of R_p will be too low and the calculated corrosion rate will be too high. Care has to be taken in the interpretation of R_p data for corrosion systems in which localized corrosion is the main corrosion mechanism. For these systems, the experimental R_p data should be used only as a qualitative indication that rapid corrosion is occurring. Large fluctuations of the R_p data with time are often observed for systems undergoing pitting or crevice corrosion.

A simplification of the polarization resistance technique is the linear polarization technique[24,28] in which it is assumed that the relationship between E and i is linear in a narrow range around E_{corr}. Usually only two (E,i) points are measured and it is

often assumed that B has a constant value of about 20 mV. This approach is mainly used in field tests and forms the basis of commercial corrosion rate monitors. For the applications related to MIC, the combination of measurements of E_{corr}, the redox potential and R_p would be very useful for monitoring purposes, however, very few authors have reported the results of such investigations. R_p can also be determined as the d.c. limit of the electrochemical impedance. This approach will be discussed below in the section dealing with electrochemical impedance spectroscopy (EIS).

Applications of the polarization resistance technique have been reported by King et al.[19] in a study of the corrosion behavior of iron pipes in environments containing SRB. Other techniques used in this study were potential/time monitoring, zero resistance ammetry, electrochemical noise and a.c. impedance. The authors concluded that 'linear polarization resistance monitoring (LPRM) was the most useful technique'. In a similar study, Kasahara and Kajiyama[18] used R_p measurements with compensation of the ohmic drop and reported results for active and inactive SRB conditions. Nivens et al.[29] calculated the corrosion c.d. i_{corr} from experimental R_p data and Tafel slopes for SS 304 exposed to a seawater medium containing the non-sulfate-reducing bacterium *Vibrio natriegens*.

Mansfeld et al.[30] have used the linear polarization technique to determine R_p for mild steel sensors embedded in concrete. The concrete samples were exposed to a sewer environment in Los Angeles County for about nine months. One sample was periodically flushed with sewage in an attempt to remove the acidic environment produced by the biofilm, the other sample was used as a control. A special data logging system was used to collect R_p data at 10 min intervals simultaneously for the two corrosion sensors and two pH electrodes which were placed on the concrete surfaces. Figure 5 shows the cumulative corrosion loss Σ INT, where INT was obtained by integration of the $1/R_p$–time curve as:

$$INT = \int_{t_1}^{t_2} dt/R_p. \tag{5}$$

A qualitative measure of the corrosion rate can be obtained from the slope of the curves in Fig. 5. The integrated corrosion loss INT is given in Fig. 5 units of ohm^{-1}. Due to the presence of the uncompensated ohmic resistance and the lack of values for the Tafel slopes (equation 3), the data in Fig. 5 should be viewed only as indicative of significant changes in corrosion rates. The corrosion loss remained very low during the first two months and then showed a large increase for both samples. This increase occurred at about the same time that the surface pH reached very low values of 1 or even less. The total corrosion loss as determined from the integrated R_p data was less for the control than for the flushed sample. These results were confirmed by the EIS data shown below which were obtained for the two systems at the end of the field test.

The dual-cell technique

The dual-cell or split-cell technique developed by Little et al. for the study of MIC[1,31] allows continuous monitoring of the changes in the corrosion rate of a metal due to the presence of a biofilm. In this technique two identical electrochemical cells are biologically separated by a semipermeable membrane. The two working electrodes are connected to a zero resistance ammeter (ZRA) or a potentiostat set to an applied potential of 0 mV. Bacteria are then added to one of the two cells and the
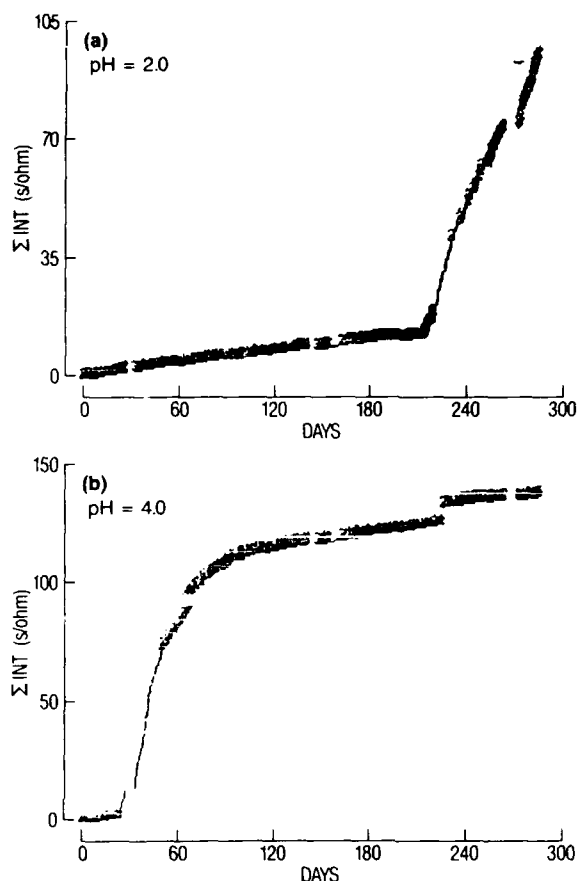
Fig. 5. Integrated corrosion loss Σ INT for mild steel sensors embedded in concrete.[30]

resulting galvanic current is recorded on a strip chart recorder to provide a continuous record of the time dependence of the corrosion process. The sign and the magnitude of the galvanic current can be used to determine details of the corrosive action of the bacteria. It has to be recognized that the galvanic current is a measure of the increase of the corrosion current of the anode due to the coupling to the cathode and does not allow calculation of the corrosion rate of either electrode in a simple manner.[32] In each experiment with the dual-cell technique it has to be established that current flow does not occur between supposedly identical electrodes. Additional mechanistic information could be obtained if the potential of the galvanic couple were also to be recorded as a function of time.

Daumas et al.[33] have used the concept termed a 'biological battery' to study the corrosion mechanism of K55 steel in the presence of hydrogenase-containing (Hase⁺) and non-hydrogenase (Hase⁻) bacteria. Figure 6 shows the galvanic c.d. between a sterile cell and an inoculated cell in the presence of SRB Hase⁻ (curve A) and in the presence of SRB Hase⁺ (curve B). The authors concluded based on these results and others obtained in the absence and presence of sulfide that the oxidation of cathodic hydrogen by the bacteria was the dominant corrosion mechanism for the

Hase[+] organisms. They suggested that FeS played an important role in the corrosion reaction with Hase[-] organisms.

Little et al.[31] have used the split-cell technique to simulate the oxygen-deficient or even oxygen-free conditions which occur under biofilms when oxygen is taken up by the respiring microorganisms as rapidly as it diffuses to the metal surface. When oxygen was bubbled though both cells with Ni 201 as working electrodes, the galvanic current remained at zero. Similarly, no current flow was observed when nitrogen was passed through one cell at 23°C (Fig. 7). However, when the temperature was raised to 60°C under the same conditions the electrode in the deaerated compartment became the anode due to complete removal of oxygen (Fig. 7). Other applications of the dual-cell techniques can be found in Refs 34–36.

Electrochemical impedance spectroscopy

EIS is a relatively new technique in corrosion research which has found many successful applications. A recent summary of the background of EIS and applications in many areas of electrochemistry can be found in the proceedings of the First International Symposium on EIS which was held in 1989.[37] Mansfeld has discussed some basic concepts concerning the recording and analysis of impedance data[38,39] and with Lorenz has compared the results obtained with a.c. and d.c. techniques for iron in the presence of corrosion inhibitors.[40]

In the EIS technique the impedance data are recorded as a function of the frequency of the applied signal at a fixed working point (E,i) of a polarization curve. In corrosion studies this working point often is the corrosion potential ($E = E_{corr}$, $i = 0$). Usually a very large frequency range has to be investigated to obtain the complete impedance spectrum. In most corrosion studies this frequency range extends from 65 kHz, which is the upper limit of a commonly used frequency response analyser (FRA), to 10 mHz. The impedance data are usually determined with a three-electrode system, although it is also possible to use a two-electrode system in which both electrodes are of the same material. A potentiostat is used to apply the potential at which the data are to be collected. The FRA is programmed to
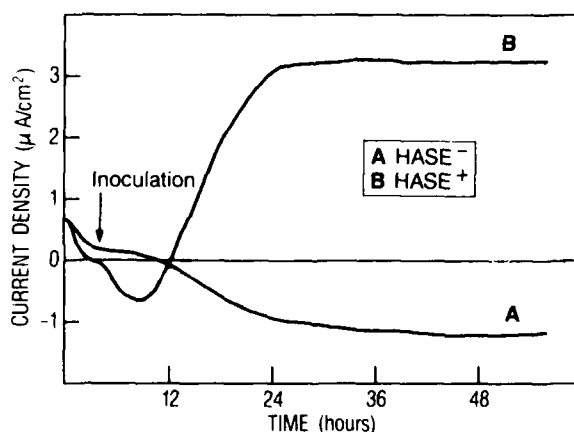

Fig. 6.   Time dependence of the galvanic current in the presence of SRB Hase[-] (curve A) and SRB Hase[+] (curve B).[31]
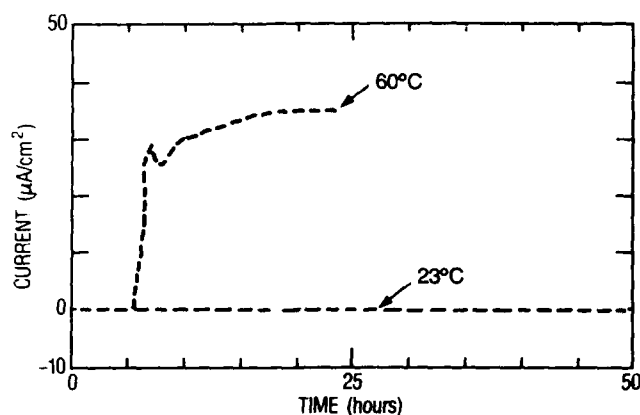
FIG. 7. Time dependence of the galvanic current resulting from abiotically created differential aeration.[31]

apply a series of sine waves of a constant amplitude, which needs to be small enough to remain in the linear potential region, and varying frequency. The impedance data are determined by the FRA at each frequency and stored in its memory. Since a very large number of data has to be collected, displayed and analysed it is essential to use adequate software for these purposes.

The type of information obtained with EIS differs from that determined with the other techniques described in this review since the corrosion system is analysed at a fixed potential (or current). The properties of the system at this potential can then be determined through the analysis of the frequency dependence of the impedance. One of the advantages of EIS is the fact that only very small signals are applied. In many cases, EIS data have shown that existing models for corrosion systems based on results of studies with d.c. techniques were too simplistic. Only when all details of an impedance spectrum can be explained in the entire frequency range can one be satisfied that the model employed is indeed correct. The inhomogeneous surface model proposed by Juettner et al.[41] is a good example for the development of a model which explains the coupling of charge transfer and mass transport reactions in a supposedly simple system such as the corrosion of iron in neutral aerated media. A very important point in the use of the EIS technique is the development of software for the analysis of the experimental data. Such software needs to be tailored to the particular system to be studied as will be shown for the analysis of data obtained for calcareous deposits on stainless steels.

Several reports have already been published in which EIS has been used for the study of MIC. The evaluation of some of these reports is often made difficult by the unfortunate tendency to display the impedance data using linear coordinates in complex plane plots. As pointed out elsewhere,[42] this approach neglects the fact that the impedance often changes over many orders of magnitude and that the frequency dependence of the impedance cannot be recognized in complex plane plots. The preferred format for the display of EIS data is therefore the Bode-plot in which log |Z| and the phase angle are plotted vs the frequency (f) of the applied signal with |Z| being the modulus of the impedance. Often the EIS-data have been only used to

determine the polarization resistance R_p which is defined as the d.c. limit of the real part of the impedance:

$$R_p = \lim_{f \to 0} \{Re(Z)\} - R_u, \tag{6}$$

where R_u is the solution resistance. In this case all the other important information contained in the impedance spectrum is ignored.

Several applications of EIS are contained in the *Proceedings of the International Conference on Biologically Induced Corrosion*. These papers deal with the role of SRB in the corrosion of buried pipes[18,19] and reinforced concrete.[47] The analysis of these data is qualitative and no models for the impedance behavior in these complicated systems have been presented. Dowling *et al.* have studied the effects of MIC on stainless steel weldments in artificial seawater using EIS, small amplitude cyclic voltametry and ESCA.[43] From the frequency dependence of the impedance data it was concluded that two relaxations were associated with the as-welded inoculated surface, while only one time constant was detected in the Bode-plots for the as-welded sterile surface or the polished surfaces.[43] The authors speculated that the occurrence of a second time constant was due to the development of pits. Dowling *et al.*[44] have also used EIS to study the corrosion behavior of carbon steels affected by bacteria. Attempts were made to determine R_p from the EIS data.

The formation of the biofilm and calcareous deposits on three stainless steels and on Ti grade 2 during exposure to natural seawater has been followed using EIS and surface analysis with SEM/EDAX by the groups of Mansfeld and Little.[16] Samples were either exposed at E_{corr} or polarized at -850 mV(SCE) for certain time periods and then removed for analysis. Figure 8 shows a typical example for the type of data obtained for the unpolarized samples. The impedance is dominated by the capacitive component. No changes in the shape of the spectra were detected as the biofilm formed with increasing exposure time. Figure 9 shows the time dependence of the electrode capacitance (C_{dl}) for the four materials. The small decrease of the capacitance with time could be due to the formation of the biofilm which was shown by observation with SEM to be of a patchy nature.[16]

Much more pronounced changes in the impedance spectra were observed for the polarized samples. Figure 10 gives spectra at three different exposure times for

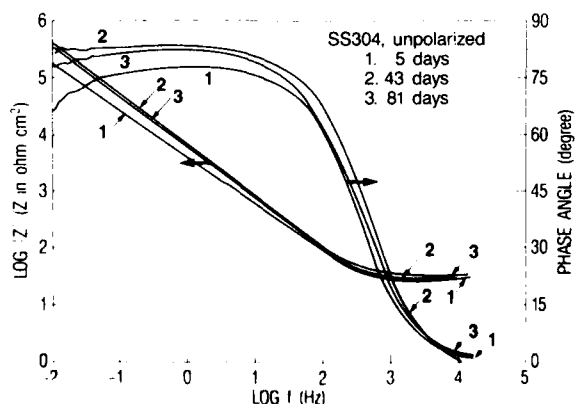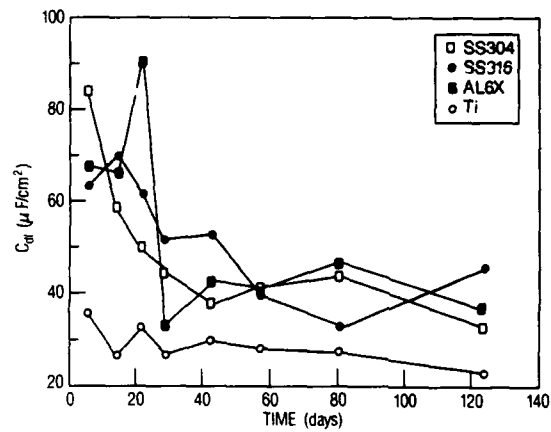Fig. 8.   Bode-plots for unpolarized SS 304 exposed to flowing natural seawater for different time periods.[16]

FIG. 9.   Time dependence of the electrode capacitance C_{dl} for unpolarized stainless steels
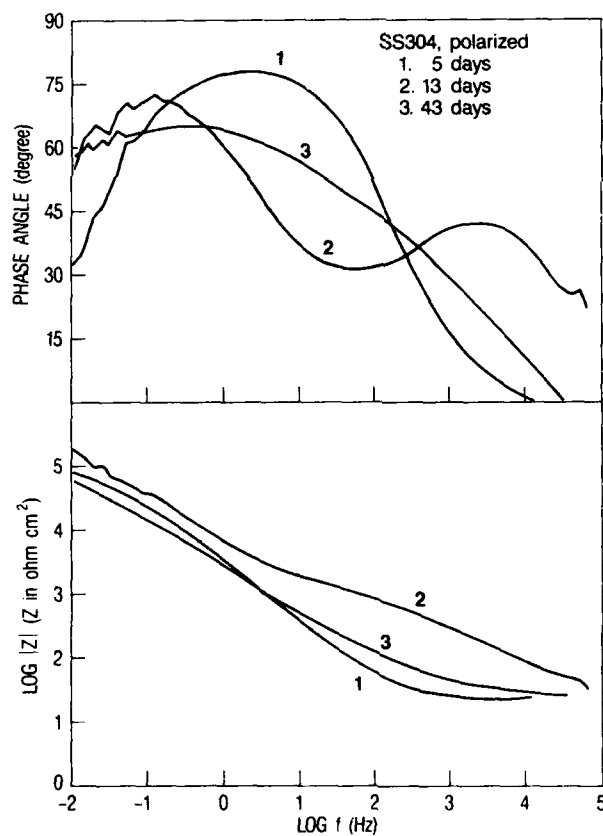and Ti grade 2 exposed to flowing natural seawater. [16]

FIG. 10.   Bode-plots for SS 304, polarized to -850 mV(SCE), as a function of exposure
time to flowing natural seawater. [16]
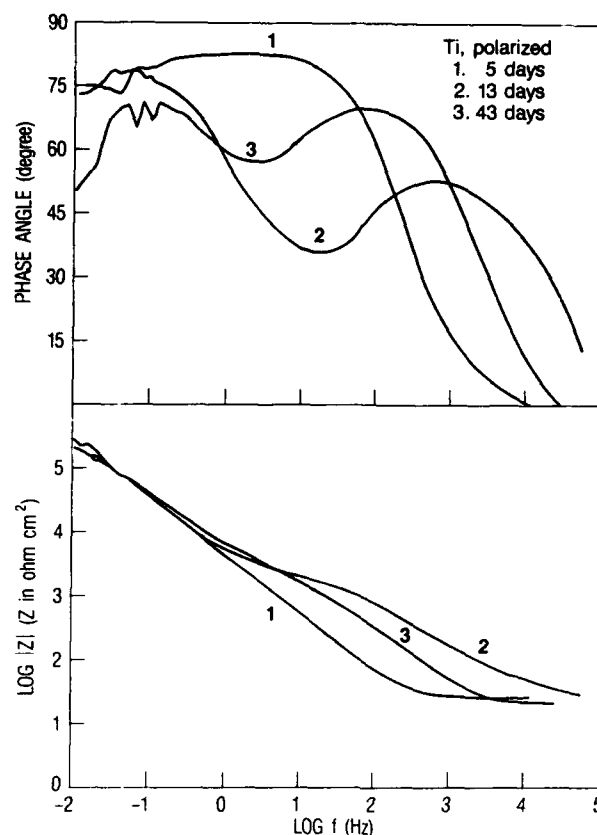
F. MANSFELD and B. LITTLE

FIG. 11.   Bode-plots for Ti grade 2, polarized to −850 mV(SCE), as a function of exposure
time to flowing natural seawater.[16]

SS 304. Similar data were obtained for SS 316 and AL6X. At very short exposure
times one time constant was observed, similar to the data for the unpolarized
samples. As the calcareous deposit was formed, a second time constant appeared due
to the presence of this porous deposit. SEM analysis showed that the area which was
not covered by the calcareous deposit was partially covered by bacteria. When the
calcareous deposit covered the entire surface and its porosity became quite small, the
time constant at the higher frequencies disappeared again. The data for Ti grade 2
after 43 days were different from those for the stainless steels insofar as two time
constants were still apparent (Fig. 11). This behavior was explained by the different
morphology of the calcareous deposit on Ti using the model for the impedance of a
porous polymer film on metals.[45] A full analysis of the data with the COATFIT
software is given elsewhere.[16] It is remarkable that the predictions concerning the
differences in the structure of the deposits for the stainless steels and Ti are fully
confirmed by the SEM data as shown in Fig 12

Mansfeld and Shih have shown recently that EIS can be used to detect the
initiation and growth of pits on Al alloys as well as on Al-based metal matrix
composites.[46] This possibility would be very useful for the study of MIC, where many
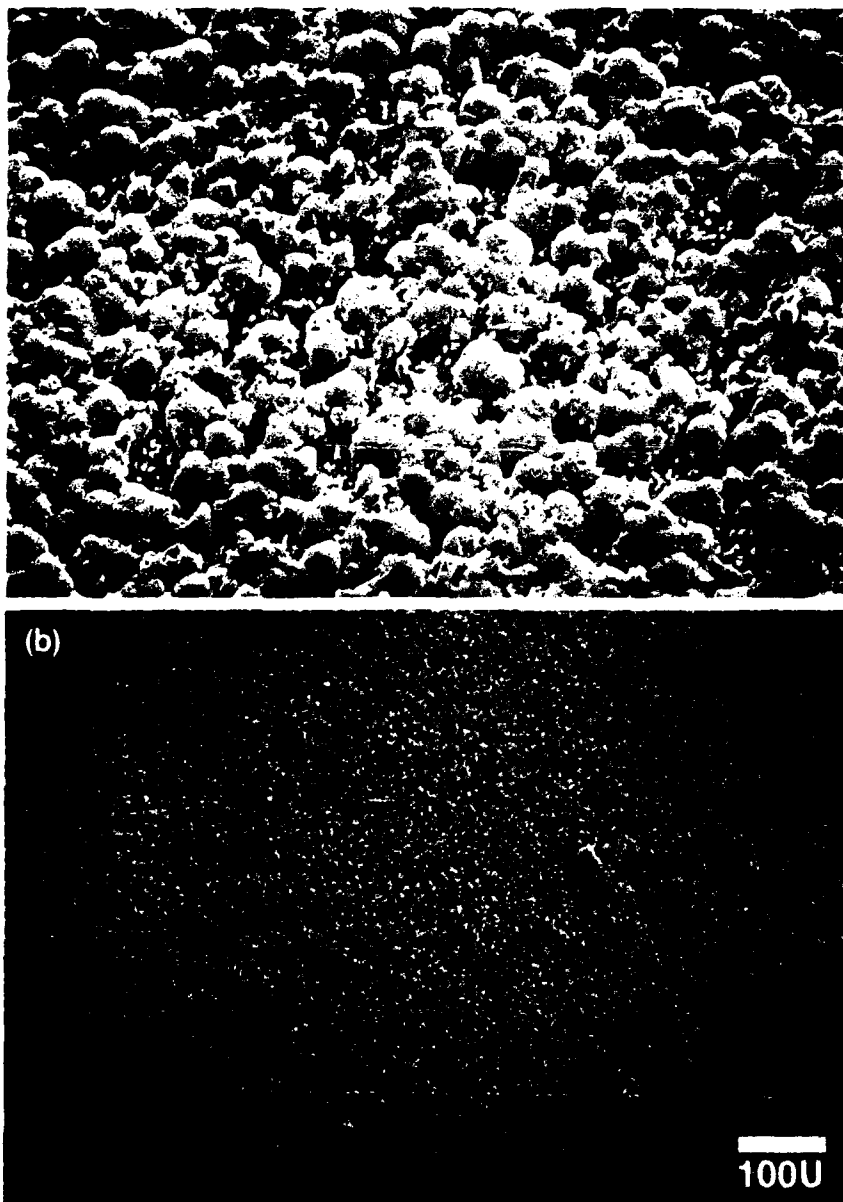corrosion reactions are considered to occur because of the localized action of

FIG. 12.   Surface of (a) SS 304 and (b) Ti grade 2 after polarization to −850 mV(SCE) in flowing natural se ·water for 43 days. [16]
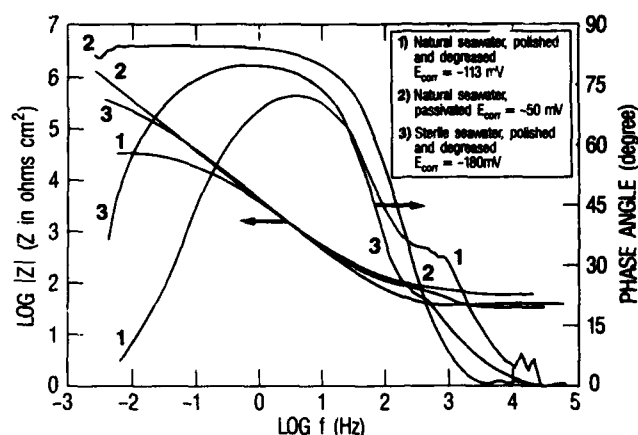
261

FIG. 13. Bode-plots for SS 304 exposed to natural seawater (curves 1 and 2) and to pasteurized, filtered seawater.[17]

microorganisms. In the study of stainless steels and Ti exposed to seawater, no signs of localized corrosion were detected visually or by EIS over the entire test period of more than four months. However, in laboratory tests conducted in seawater, large changes in the shape of the impedance spectra were observed when a faulty O-ring was used which created crevice corrosion of SS 304. Curve 1 in Fig. 13 shows the type of spectra which were recorded in the presence of crevice corrosion.[17] Two time constants dominate the spectrum in this case as can be seen by the occurrence of a peak in the phase angle at frequencies between 100 and 1000 Hz. R_p has decreased to about 3×10^4 ohm cm^2. The surface pretreatment for the sample in curve 1 consisted of polishing and degreasing. When the surface was passivated by immersion in concentrated HNO_3, crevice corrosion did not occur and only one time constant was observed (curve 2). Some deviations from capacitive behavior were also detected for a sample which was exposed to sterilized seawater by the changes of the impedance between 100 and 1000 Hz indicating the initiation of localized corrosion. Care has to be taken not to interpret these impedance data as being due to the formation of a porous biofilm.[17]

Impedance measurements have confirmed the conclusions discussed above for the corrosion monitoring effort in a corrosion chamber fed by sewer gases (Fig. 5).[30] After the field tests had been terminated the samples were returned to the laboratory and EIS-data were collected after immersion in tapwater for 48 h. The impedance data were determined for the two-electrode system at $E_{appl} = 0$ mV. As shown in Fig. 14, the impedance at the d.c. limit and therefore also R_p were lower for the mild steel sensors which were embedded in the concrete samples flushed periodically with sewage. This result is in agreement with the R_p data collected independently on the basis of the linear polarization resistance technique (Fig. 5).[30]

Electrochemical noise analysis

In electrochemical noise measurements the fluctuations of the potential, often E_{corr}, or the current are determined as a function of time or the experimental conditions. One of the advantages of this technique is that no external signal needs to

be applied for the collection of the noise data. In some cases the potential of a test electrode is measured versus a stable reference electrode whereas in others the noise data are recorded for two electrodes of the same material which are exposed under identical conditions. In principle, a statistical analysis of the noise data can provide information concerning the nature of the corrosion processes and the magnitude of the corrosion rate. However, most analyses of electrochemical noise measurements have been qualitative and used to determine the occurrence of localized corrosion. The frequency and the amplitude of the fluctuations are sometimes used to estimate the value of the corrosion rate. The results reported so far for the application of electrochemical noise measurements suggest that this technique at its present state of development is more suited for monitoring purposes than for mechanistic studies.

A very useful approach for corrosion monitoring is that used by the research groups at the University of Manchester Institute of Science and Technology (UMIST), who combined impedance and electrochemical noise measurements in a series of experiments which were designed to simulate conditions in concrete oil storage tanks.[47] The effects of SRB and other communities of microorganisms on the corrosion of concrete and the steel reinforcement were studied. The authors used a portable multi-channel instrument which also performed zero resistance ammetry.[47] The electrochemical noise data were collected with a microvoltmeter and a computer which collected time records consisting of 1024 potential readings taken at one second intervals. These data were converted to the frequency domain and then subjected to a statistical analysis. Moosavi et al.[47] presented their results for a reinforced concrete block exposed to a marine medium containing active SRB in two noise plots: a time record and a potential distribution chart showing the population and the magnitude of the potential fluctuations. The data were collected at E_{corr}. The time record after 218 days for the covered rebar reveals events that could be due to sudden rupture of the protective oxide film followed by immediate repassivation (Fig. 15). The events recorded for the exposed rebar showed fluctuations, however, their magnitude was about a factor of 10 lower (Fig. 16). King et al.[19] interpreted their results obtained with noise measurements for steel pipes in environments
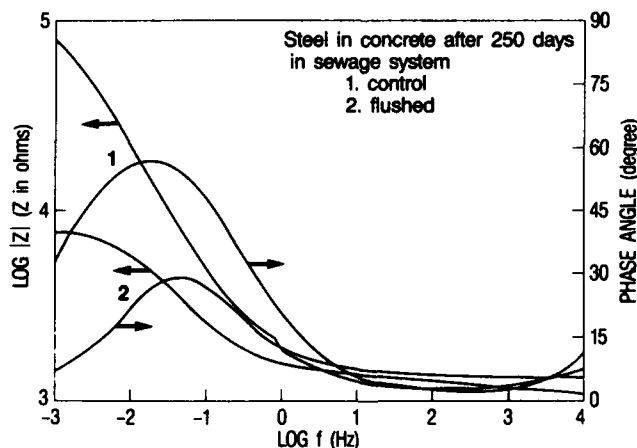
FIG. 14.   Bode-plots for mild steel embedded in concrete after 250 days exposure in a corrosion chamber fed with sewer gas; curve 1: control, curve 2: flushed periodically with sewage.[30]
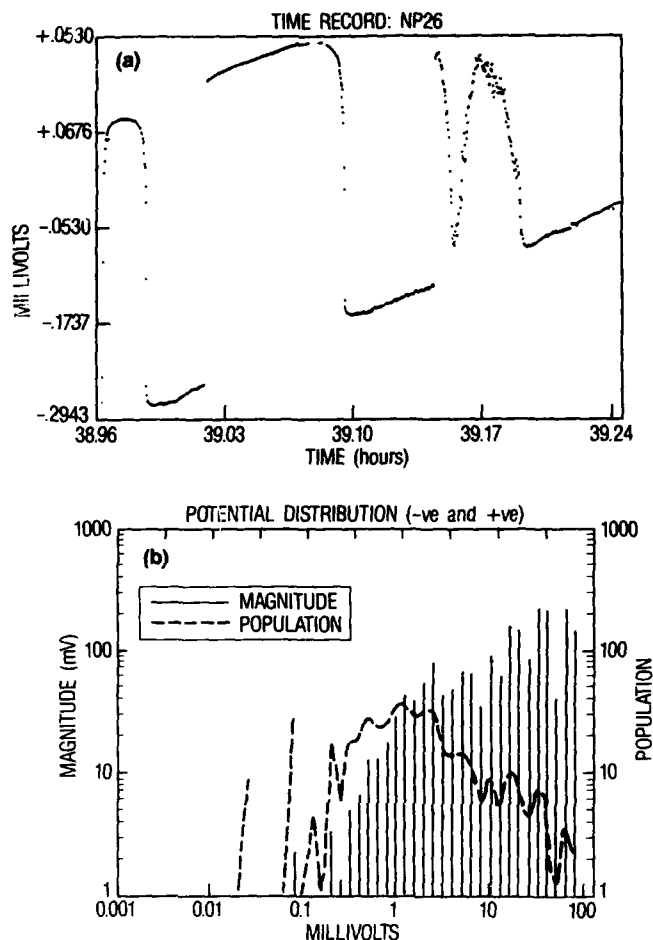
FIG. 15.   Time record after 218 days for covered reinforcements in media containing active cultures of SRB.[47]

containing SRB as being indicative of film formation and breakdown as the probable mechanism of corrosion. Similar conclusions had been reached from the analysis of their zero resistance ammetry data.[19] In the analysis of noise data such as those shown in Figs 15 and 16 it has to be considered that the magnitude of the noise fluctuations depends on the total impedance of the system. A corroding metal undergoing uniform corrosion with fairly high corrosion rates might be less noisy than a passive metal which shows occasional bursts of noise due to localized breakdown of the film followed by rapid repassivation.

The experimental approach of Iverson reported in 1968[48] differs from that described above insofar as the test specimen is coupled to a Pt electrode and the noise is measured across a resistor between the two electrodes. In this case the test electrode was polarized to an unknown extent and the measured noise might be a result of this polarization. This limitation of Iverson's approach was not reported by Dexter et al.[3] in their recent review which seemed to suggest that all noise

measurements are carried out in this manner. Nevertheless, Iverson et al.[49] have obtained potential noise data in the laboratory for mild steel in a trypticase–seawater culture of the marine strain of *Desulfovibrio* and in the field for a gas transmission line. The authors concluded that breakdown of the iron sulfide film may be accompanied by the generation of electrochemical noise. They also were suggesting further development of the noise technique for monitoring purposes.

Large signal polarization techniques

In the experimental techniques described above, measurements are carried out without the application of an external signal (E_{corr}, dual-cell technique, electrochemical noise) or with the application of only a very small perturbation (R_p, EIS). The large signal polarization techniques employ potential scans which can range from several hundred mV to several V. The recording of a polarization curve provides an overview of the types of reactions which occur for a given corrosion system such as charge transfer or diffusion controlled reactions, passivity, transpass-
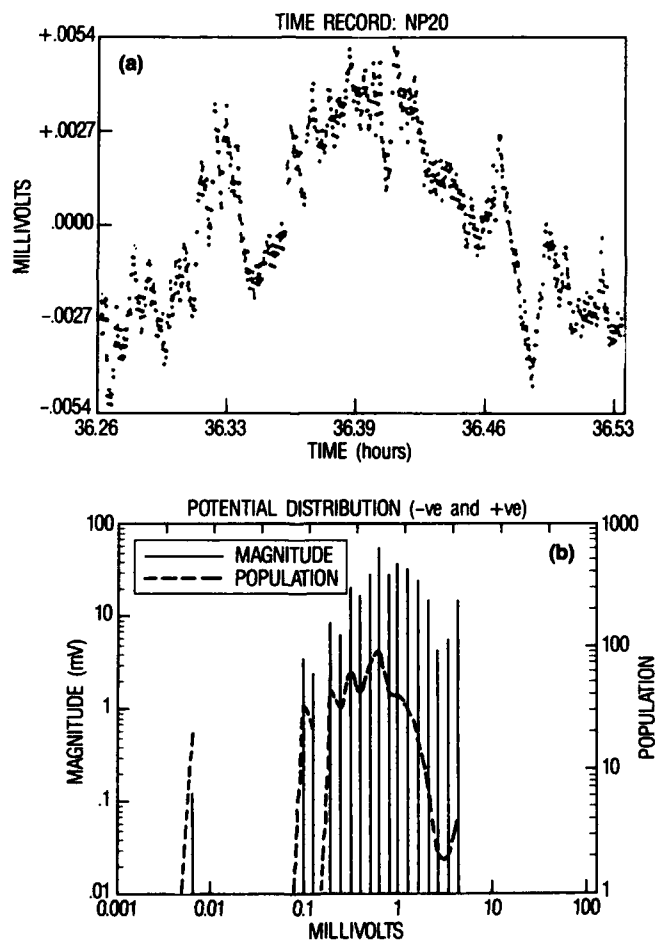

Fig. 16. Time record after 218 days for exposed reinforcements in media containing active cultures of SRB.[47]

ivity and localized corrosion phenomena. The effects of alloying or the addition of inhibitors can be recognized in the changes of the polarization curves. While the recording of potentiodynamic polarization curves seems to be very simple, especially if commercially available software is used, it has to be remembered that the experimental conditions have to be tailored to the electrochemical characteristics of the system under study to obtain optimum results. The choice of the correct sweep rate and the elimination of the ohmic drop during the experiment are important considerations as discussed elsewhere.[50] The use of excessive sweep rates as in the 'corrosion behavior diagrams' obtained by the rapid scan potentiodynamic polarization technique[3] reflects the effects of the experimental conditions on the shape of the polarization curves, but does not result in any meaningful mechanistic data. Polarization over wide potential ranges can drastically alter the properties of the surface under investigation. Therefore separate samples should be used for the recording of anodic and cathodic polarization curves and each sample should only be used once. Quantitative information which can be obtained from polarization curves includes the values of the Tafel slopes b_a and b_c, the corrosion c.d. i_{corr}, the values of the diffusion limited c.d. for hydrogen reduction i_{1,H_2} and oxygen reduction i_{1,O_2} and parameters related to passivity such as the critical potential E_{crit} and critical c.d. i_{crit} for passivation and the passive c.d. i_{pass}. Additional parameters such as the pitting potential E_{pit} and the protection potential E_{prot} are related to the susceptibility of a metal to localized corrosion. Since the recording of polarization curves is a well-established technique covered in many text books and in ASTM Standard Recommended Practices such as G3, G5, G59 and G61, no further discussion concerning the details of experimental procedures is needed here.

Numerous investigators have used the recording of polarization curves to determine the effects of microorganisms on the electrochemical properties of metal surfaces and the resulting corrosion behavior. In most of these studies comparisons have been made between polarization curves recorded in sterile media with those obtained in the presence of bacteria and fungi. Early studies of MIC of mild steel were reviewed by Costello, who in 1969 provided a survey of the literature.[51] Recently Tiller[52] reviewed the European research effort on microbial corrosion between 1950 and 1984. His paper contains 21 references to the use of polarization curves for the interpretation of the impact of SRB on mild steel. A further review of polarization techniques applied to MIC has been given by Duquette and Ricker[53] who among others cited the work of Salvarezza and Videla[54] and Obuekwe et al.[55,56] While there is no general agreement concerning the details of the corrosion mechanisms, most authors suggest that the observed increase of corrosion rates is due to the influence of the microorganisms on the rates of the anodic and/or cathodic reactions involved in the corrosion process.

The complexity of the naval brass/polluted seawater interface was demonstrated by Deshmukh et al.[57] who discussed the influence of sulfide pollutants based on the results obtained with potentiodynamic polarization curves. The shape of the anodic polarization curve was drastically changed in the presence of sulfides or SRB (Fig. 17). E_{corr} became substantially more negative. An active–passive transition and hysteresis in the reverse scan were observed. An interesting application of polarization techniques has been given by de Mele[58] in an evaluation of the biodeterioration of implant material including aluminum in human plasma and silver in saline solution containing Na_2S.
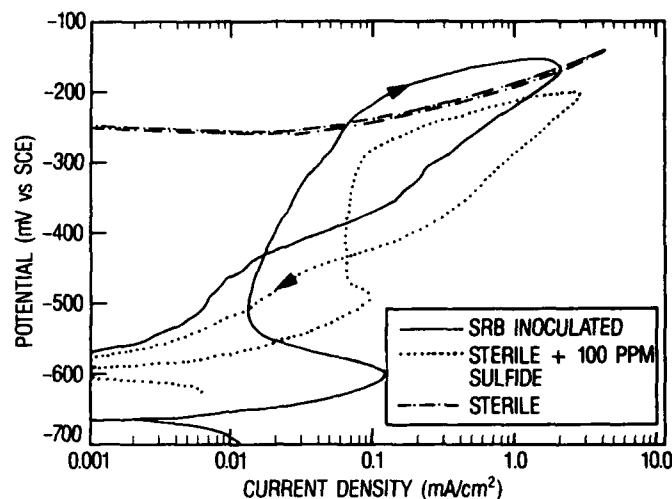
FIG. 17.   Potentiodynamic polarization curves for naval brass in seawater media.[57]

Polarization techniques have also been used in attempts to determine the mechanism by which microorganisms induce localized corrosion in the forms of pitting or crevice corrosion. In most cases the pitting potential E_{pit} has been determined in the presence and absence of bacteria. At this point it has to be considered that the pitting potential E_{pit} provides only the tendency for pitting, but does not give information concerning the rate at which pits propagate. For Al alloys in sterile 3% NaCl it was found that Al 2024 has a more noble E_{pit} than Al 1100, Al 7075 or Al 6061, however the localized corrosion rate was the highest for Al 2024. The extent of pitting cannot be predicted from E_{pit} data alone.

Salvarezza et al.[59,60] have used several isolates obtained from jet fuel storage tank sludges to obtain information concerning the influence of different microorganisms on the corrosion process of Al alloys in fuel–water systems. The authors concluded that E_{pit} could be used to determine the importance of each biological species in the corrosive attack of the Al alloys. Rosales et al.[61-64] have determined the influence of microbial contaminants in aircraft fuel, alloying elements and surface heterogeneities on the nucleation and propagation of pitting of Al 7075 and have concluded that the electrochemical tests reproduced the corrosion problems which were observed in service conditions.

The experimental conditions used to record a pitting scan can affect the value of E_{pit}. If the scan rate is too high, E_{pit} will usually be higher than the value determined under steady-state conditions. Likewise the experimental value of E_{prot} becomes more negative if the c.d. at which the scan is reversed is increased. Because of these problems, E_{pit} has been determined sometimes by a constant-potential technique in which a series of increasing anodic potentials is applied and the current is measured as a function of time. If the current decreases continuously at an applied potential E, it is concluded that E is more negative than E_{pit}. By increasing E stepwise, E_{pit} can be determined. Very few applications of this very useful approach can be found in the literature for the study of MIC phenomena. Videla[65] has used this technique in a study of the action of Cladosporium resinae growth on the electrochemical behavior

of aluminum. Current transients at different potentials were compared for Al 2024 in 0.01 M NaCl and in 0.01 M NaCl + 0.05 M citric acid (pH = 2.5). These data suggest that E_{pit} in 0.01 M NaCl was between -0.55 and -0.50 V(SCE) and was more positive than -0.55 V in the solution of pH = 2.5. These results confirm that E_{pit} depends on pH. It should be noted that a printing error[65] which was copied in the Dexter et al. review[3] might make it difficult to analyse Videla's data.[65] Curve a in Fig 3[65] was measured at -0.55 V as in Fig. 4 rather than at -0.05 V as stated in the figure caption for Fig. 3.[65]

Ringas and Robinson[66] have performed electrochemical tests on several stainless steels and on mild steel in three cultures of SRB. In all cases the pitting resistance was lower in cultures of SRB. Figure 18 shows potentiodynamic polarization curves with a reversed scan for SS 316 in sterile medium and in strain 8303.[66] In the sterile medium, the alloy was passive and displayed a large passive range. The reverse scan showed that active pits were not formed. The shape of the anodic polarization curve was very different in the bacterial culture. E_{corr} was more active, an active–passive transition was observed and the passsive c.d. was higher suggesting that the passive film formed in the bacterial culture was less protective. The reverse scan showed that active pits had been formed which did not repassivate. Similar results were shown for SS 409 and 430.[66] The authors concluded that sulfide-induced pits were initiated at more negative potentials than those initiated by chlorides. Additional studies by these authors[67] involved total immersion in cultures of SRB and surface characterization with SEM. The results of this study agreed with those from the electrochemical tests.[66]

SUMMARY AND CONCLUSIONS

The authors of this review would expect the reader who has followed their discussion to this point to pose the obvious question: 'Are electrochemical techniques helpful for the study of MIC?' A general answer by the authors would be:
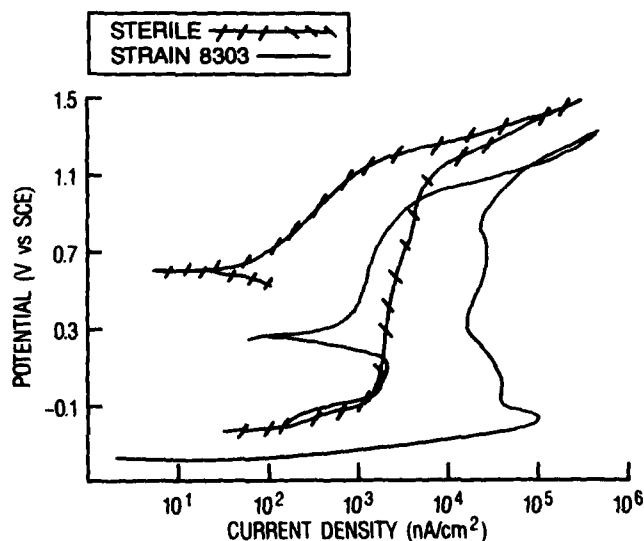

Fig. 18. Pitting scans of SS 316 in sterile medium and strain 8303.[66]

'Yes'. The details of the positive answer depend, however, on the particular interests of the person asking the question. Obviously in an area of corrosion as complicated as MIC, one single technique cannot be expected to provide all the answers which are needed for the establishment of mechanisms. As in other fields of corrosion, inputs are needed from other disciplines. A case in point would be the phenomena of stress corrosion cracking or corrosion fatigue, where electrochemical tests have provided answers to explain the results of experiments based on the concepts of fracture mechanics. The most productive use of electrochemical techniques in basic research in the field of MIC would be in providing answers to questions posed by the experts in the fields of microbiology and corrosion.

In judging the usefulness of electrochemical techniques for the evaluation of MIC, it should not be forgotten that many billions of dollars which have been invested in the equipment of oil refineries, chemical plants and other facilities are protected from corrosion including MIC by electrochemical monitoring techniques such as the linear polarization technique. This very simple concept has found worldwide acceptance as a monitoring tool in which the exact details of the corrosion mechanism might sometimes not be too well understood, but where the experience of the responsible corrosion engineer suggests the steps which are needed to avoid a costly corrosion problem. With further investments in basic research concerning the applications of electrochemical techniques in the study of MIC combined with microbiological and surface analytical techniques, similar success should evolve quickly in basic research and practical applications.

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